

Molecular Dynamics Simulation of Thermal and Thermodynamical Properties of ThO₂

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Abstract—Nuclear energy has become a very important source of energy, realising the low efficiency and low productivity of fossil fuels. The nuclear fission process generates heat which is further removed by the coolant and using steam and turbines, electrical energy is produced. And for a stable fission reaction, nuclear reactor design and fuel composition alongwith storage of spent fuel and its reprocessing need to be studied, both theoretically and experimentally (if possible). Molecular Dynamics Simulation is an atomistic approach towards predicting the behavior of materials using the classical equations of motion (Newton's Laws of Motion). This paper showcases the close results produced by the simulation by using two inter-atomic potential set of parameters for ThO₂. One is Buckingham potential and the other being Buckingham-Morse-Many Body potential. ThO₂ based materials are important fuel for various reactor systems (conventional Pressurised Water Reactors (PWR), Advanced Heavy Water Reactors (AHWR)) owing to a number of neutronic properties. Hence, it clearly needs an experimental database of properties like melting point, density, thermal expansion and thermal conductivity in order to meet the fuel requirements. However, due to extensive as well as expensive safety precautions, not all the properties can be determined at every required temperature experimentally. Hence, classical Molecular Dynamics (MD) is an efficient simulation technique to obtain the same. It was observed that Linear Thermal Expansion parameter was predicted very accurately by both the potentials. Moreover, Melting Point as well as single crystal elastic constants' prediction was very close to the experimental value.

Index Terms— Buckingham potential, Buckingham-Morse-Many-Body potential, Two-Phase Simulation, Super-ionic transition, MSD (Mean Square Displacement), RDF (Radial Distribution Function)

1. INTRODUCTION

NUCLEAR power releases energy stored within the nucleus of an atom, contributing to a rise in reactor temperature that can be utilized in much the same way as in any conventional power plant. In the past decade, there has been a renewed interest in studying the feasibility of thorium-based materials as a fuel for various reactor systems (conventional Pressurised Water Reactors (PWR) and thermal breeder reactors, e.g. Advanced Heavy Water Reactors (AHWR) owing to a number of superior material and neutronic properties [8,9]. During use in a nuclear reactor the fuel properties are altered significantly due to fission and reactor conditions. This underpins the fuel performance and effectively limits the amount of energy that can be extracted before it must be removed from the reactor. Knowledge of the variation in the thermal, mechanical, chemical and physical properties of nuclear materials can be very closely provided if we simulate the materials in the desired environment. This knowledge helps us in predicting the behavior of materials during defect formation, propagation, etc. and also for the behavior of materials under high temperature and pressure conditions. Taking appropriate potentials, phase stability among the polymorphs can also be predicted. Here, an atomistic approach has been followed through Molecular Dynamics Simulation. It is done to study the evolution of a system of N particles under conditions of interest. In these simulations, classical equations of motion are integrated to generate the trajectory of the particles. The N-body force equation used is:

$$m_i \ddot{r}_i = - \sum_{i \neq j, j=1}^N \nabla_i E$$

where r_i is the position vector of the i th particle, m_i is the mass of the i th particle and E is the total potential energy of the system.

In ThO₂, two sets of potential having functional form Buckingham (Buck) and Buckingham-Morse-Many-Body (B-M-MB) potential were studied for calculating mechanical, thermal and thermodynamical properties. The Linear Thermal Coefficient has been computed by calculating lattice parameter for ThO₂ with increments in temperature at an interval of 100 K. Linear Thermal Expansion Coefficient predictions by both the potentials were nearly same. On comparing, our MD calculated single crystal elastic constants showed that though Buck potential was able to predict C_{11} and C_{12} very correctly, yet B-M-MB potential predicted C_{44} very correctly. Specific Heat Capacity of ThO₂ has been calculated from the enthalpy increment data for the same. In terms of calculation of temperature of Melting Point, Buckingham potential was not able to predict the values better than the B-M-MB potential as Buck potential predicted a range between 3800-3825 K whereas B-M-MB predicted between 3650-3675 K and the experimental value lies close to 3670 K.

2. THEORETICAL METHODOLOGY

2.1. Inter-atomic potentials

For carrying out MD Simulation, the inter-atomic forces are used to predict the trajectory of atoms using Newton's Laws of Motion. These inter-atomic forces are derived from the inter-atomic potential set provided. Two types of potentials have been used in this paper.

2.1.1. Buckingham-Morse-Many-Body (B-M-MB) Potential

B-M-MB Potential combines a pair potential description of each system with the many-body EAM description of Daw and Baskes [1]. The potential energy of an atom i with respect

to all other atoms can be expressed as:

$$E_i = \frac{1}{2} \sum_j \varphi_{\alpha\beta}(r_{ij}) - G_\alpha \left(\sum_j \sigma_\beta(r_{ij}) \right)^{\frac{1}{2}}$$

Here, the pair-wise potential between two atoms α and β separated by r_{ij} is expressed by the term $\varphi_{\alpha\beta}(r_{ij})$. It includes the contribution from long-range electrostatic, $\varphi_C(r_{ij})$ and short range contributions. The second term includes Morse $\varphi_M(r_{ij})$ and Buckingham $\varphi_B(r_{ij})$ potential forms.

$$\varphi_{\alpha\beta}(r_{ij}) = \varphi_C(r_{ij}) + \varphi_B(r_{ij}) + \varphi_M(r_{ij})$$

$$\varphi_C(r_{ij}) = \frac{q_\alpha q_\beta}{4\pi\epsilon_0 r_{ij}}$$

$$\varphi_M(r_{ij}) = D_{\alpha\beta} [\exp(-2\gamma_{\alpha\beta}(r_{ij} - r_{\alpha\beta}^0)) - 2 \exp(-\gamma_{\alpha\beta}(r_{ij} - r_{\alpha\beta}^0))]$$

$$\varphi_B = A_{\alpha\beta} \exp\left(\frac{-r_{ij}}{\rho_{\alpha\beta}}\right) - \frac{C_{\alpha\beta}}{r_{ij}^6}$$

Where $A_{\alpha\beta}, \rho_{\alpha\beta}, C_{\alpha\beta}, D_{\alpha\beta}, \gamma_{\alpha\beta}$ and r_{ij}^0 are empirical parameters that describe the Buckingham and Morse potentials between atom i and j .

For cation-oxygen interactions

Coulombic, Morse and Buckingham potentials

For cation-cation as well as oxygen-oxygen

Coulombic and Buckingham potentials

The charges taken here are non-formal i.e. $q_a = Z^{eff}_a |e|$, keeping the system's charge zero. For tetravalent cations, its value is 2.2208 and for oxygen anions, its value is -1.1104.

The second term provides the sum of pair-wise functions $\sigma_\beta(r_{ij})$ between atoms i and its surrounding atoms. $\sum \sigma_\beta(r_{ij})$ is then passed through a non-linear embedding function. $\sigma_\beta(r_{ij})$ is inversely proportional to the 8th power of the inter-ionic separation with n_β being the constant of proportionality that must be empirically fitted to experimental data.

$$\sigma_\beta(r_{ij}) = \left(\frac{n_\beta}{r_{ij}}\right)^{\frac{1}{2}} (1 + \text{erf}(20(r - 1.5)))$$

The embedding function used means the many-body energy perturbation is proportional to the square root of the $\sigma_\beta(r_{ij})$ with G_α as the constant of proportionality. The total energy of atom i (E_i) is given by the sum of its pairwise interactions with the many-body perturbation due to the EAM term.

2.1.2. Buckingham Potential

$$\varphi_B = A_{\alpha\beta} \exp\left(\frac{-r_{ij}}{\rho_{\alpha\beta}}\right) - \frac{C_{\alpha\beta}}{r_{ij}^6}$$

Again, as in B-M-MB potential, the $A_{\alpha\beta}, \rho_{\alpha\beta}$ and $C_{\alpha\beta}$ are empirical parameters that describe the Buckingham potentials between atoms α and β .

For Th-Th

Parameters	Buckingham	Buckingham(in Morse-Many-Body)
A (eV/atom)	0	18600
ρ (Å)	12.0	0.2884
C (eV/Å ⁶)	0	0

For Th-O

Parameters	Buckingham	Buckingham(in Morse-Many-Body)
A (eV/atom)	26300	315.544
ρ (Å)	0.224857	0.395903
C (eV/Å ⁶)	12.8	0

For O-O

Parameters	Buckingham	Buckingham(in Morse-Many-Body)
A (eV/atom)	919.169	830.283
ρ (Å)	0.332	0.352856
C (eV/Å ⁶)	17.5296	3.884372

Morse Potential in Buckingham-Morse-Many-Body

	$D_{\alpha\beta}$ (eV)	$\gamma_{\alpha\beta}$ (Å)	$r_{\alpha\beta}^0$ (Å ⁻¹)
Th-Th	-	-	-
Th-O	0.62614	1.8596	2.49788
O-O	-	-	-

2.2. Calculation of Elastic Constants

Single Crystal Elastic Constants (C_{11}, C_{12}, C_{44}) were calculated by causing displacements (elongations and compressions) in the simulation box of ThO₂ containing 6144 atoms. The region analyzed in the simulation box was taken of prism form with tilt factor values being equal to 0.0. This was done because during the deformation, the system loses orthogonality. For C_{11} , 1.4% error for Buck potential and 4% error for B-M-MB

potential, for C_{12} , 0.2% error for Buck potential and -6.9% error for B-M-MB potential and for C_{44} , -21.5% error for Buck potential and 9.3% error for B-M-MB potential was recorded.

2.3. Fitting Curves

2.3.1. Linear Thermal Expansion Parameter

Since, the ThO_2 rods (nuclear fuel) in the reactor face high temperature conditions, they tend to expand and this expansion is studied through Linear Thermal Expansion Parameter. Simulation is being performed with the readings taken for 35 ps. This time value was derived from the lattice parameter optimization study of ThO_2 at 1500 K. A plot is made between lattice parameter \AA and temperature for temperature range 300 K to 2000 K. Values of both the co-ordinates were calculated by taking averages over the last 5 ps. The curve is befitted with a linear function $f(x)$ given by $f(x)=a+bx$.

Then using, $\alpha_p = \frac{1}{L} \left(\frac{\partial L}{\partial T} \right)_p$, the parameter was calculated. Both Buck and B-M-MB potentials predict very close value of this parameter.

2.3.2. Specific Heat Capacity (C_p)

Using simulation, for thermalization of a ThO_2 NPT ensemble at a constant temperature, we can also compute enthalpy values at every time-step. Then, taking the averages over the last 5 ps, a plot is made between Enthalpy Increment ($H'=H(T)-H(300\text{ K})$) in Jmol^{-1} and temperature in K is made. This turns out to be close to a straight line. Now, fitting a non-linear function of the type $f(x) = a + bx + cx^2 + dx^3 + ex^4 + fx^{-1}$, and using $C_p = \left(\frac{\partial H'}{\partial T} \right)_p$, C_p is computed. In order to remove the error coming in the absolute values of enthalpies, we took enthalpy increment. Here also, both Buck and B-M-MB potentials predict very close value of this parameter.

2.4. Two Phase Simulation

This technique is used in order to predict the phase stabilities between two or more phases. In the present case, it was used to determine the temperature for a first-order phase stability in which, the Melting Point range is predicted for ThO_2 . It involved an NPT ensemble consisting of 5184 atoms, which was thermalized at a 3000 K and then half the region was liquefied to 5000 K and then, the two phases (solid and liquid) were together thermalized at temperatures near the one where its RDF (Radial Distribution Function) shows a change in shape, at an interval of 100 K. And the interval is narrowed down such that on thermalizing at intermediate temperatures from the interval such that at lower temperature, the system solidifies completely and liquefies at the higher one.

2.5. MSD and RDF

The melting of O-O sub-lattice in ThO_2 at a certain temperature less than Melting Point causes changes in the properties like thermal expansion coefficient, C_p , etc. Thus, this transition also becomes an important aspect whose occurrence temperature needs to be determined. MSD (Mean Square Displacement) and RDF (Radial Distribution Function) were calculated for O-O sublattice in ThO_2 . And plots were

made for MSD in \AA^2 vs time in fs as well as RDF vs time in fs for the same. Moreover, the diffusivity of the O-O sub-lattice increases substantially on such a transition. For the two potentials, the values of the Super-ionic transition temperature are computed from the sudden change in the plots made.

3. RESULTS AND CONCLUSION

3.1. Elastic Constant

Table 1. Tabulated data for the equilibrium lattice parameter (a_0) and single crystal elastic constants (C_{11} , C_{12} and C_{44}) of ThO_2 calculated at 0 K by using the Buckingham and Buckingham-Morse-Many-Body potentials compared with experimental data.

Properties	Buckingham	Buckingham-Morse-Many-Body	Experimental
a_0 (\AA)	5.597	5.595	5.599*
C_{11} (GPa)	372.3	352.2	367.0**
C_{12} (GPa)	105.7	113.4	106.0**
C_{44} (GPa)	96.0	71.7	79.0**

* refers to [2]

** refers to [3]

Table 1 shows the data for single crystal elastic constants of the cubic ThO_2 with both Buck and B-M-MB potentials taking 6144 atoms at 0 K along-with experimental values. And it is observed that on incorporating the many-body effect in the determination of constants, the value of C_{11} and C_{12} get more deviated from the experimental values whereas, the C_{44} gets closer to the experimental value.

3.2. High Temperature Optimization

For study of the system at temperatures other than 0 K, we need to perform optimization which is required in order to minimize the fluctuations taking place.

3.2.1. Enthalpy Optimization

The main reason for fluctuations, in the physical quantities (Enthalpy, Kinetic Energy, Potential Energy, Total Energy, etc.), is the time integration algorithm that gives errors in their average calculation. These errors are greater in magnitude if the corresponding time-step is also not small. The better way to get rid of these fluctuations and drifts is to reduce the time-step which unwillingly leads to more calculations and waste of computer time.

Also, with time, these quantities tend to show lesser number of fluctuations. In order to know the number of steps after which the fluctuations in enthalpy become nominal, enthalpy (eV/atom) is plotted against time (fs) for ThO_2 at 1500 K for both potentials and the time for the minimum fluctuations to occur is noted. It came out to be approximately 25 ps. Refer Fig.1.

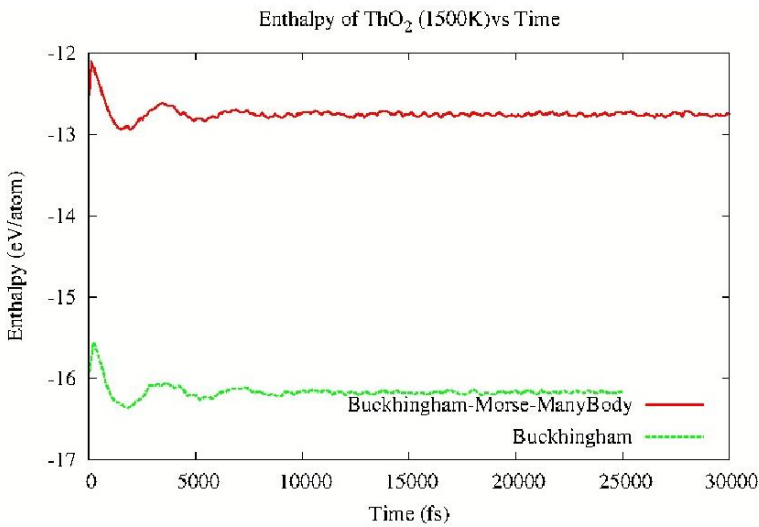
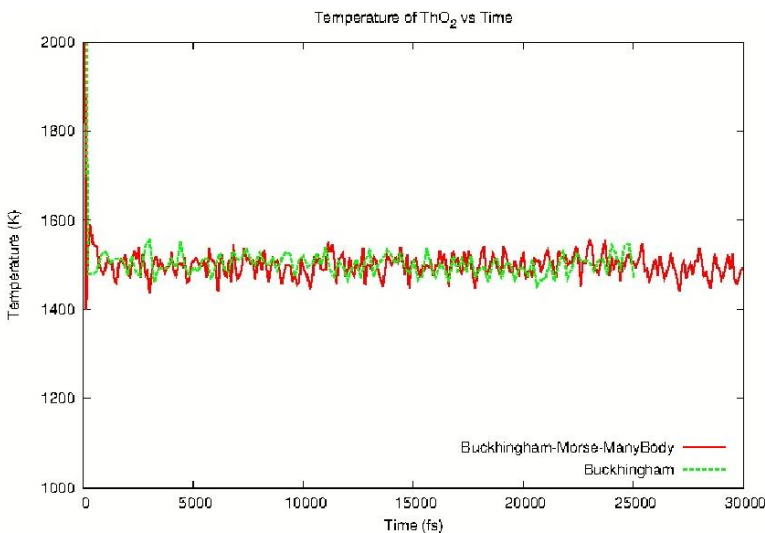


Fig.1. Enthalpy (eV/atom) being optimised at 1500 K for ThO₂ for two sets of potentials.

3.2.2. Temperature Optimization

Since temperature is related to Kinetic Energy by this relation, $K.E. = 3NKT/2$, we observe fluctuations in temperature since it's instantaneous as well as average values are derived from this relation and K.E. experiences fluctuations due to time-integration algorithm. Hence, since we need a stable value of temperature while studying the system at a certain temperature, hence fluctuations need to be minimized. Thus, in this case also, for both potentials for ThO₂ at 1500 K, optimization occurred after nearly 25 ps. Refer Fig.2.



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Fig.2. A temperature vs time plot made to check the minimum number of time-steps required in order to get an approximately constant value of temperature.

3.3. Linear Thermal Expansion Coefficient

Simulation is being performed from 300 K to 2000 K for ThO₂ with the lattice parameter being calculated at an interval of 1fs for 35000 steps. Refer Table 2. Difference in values of the coefficients can be accounted to the fact that the experimental one has been also studied for temperatures above 2000 K.

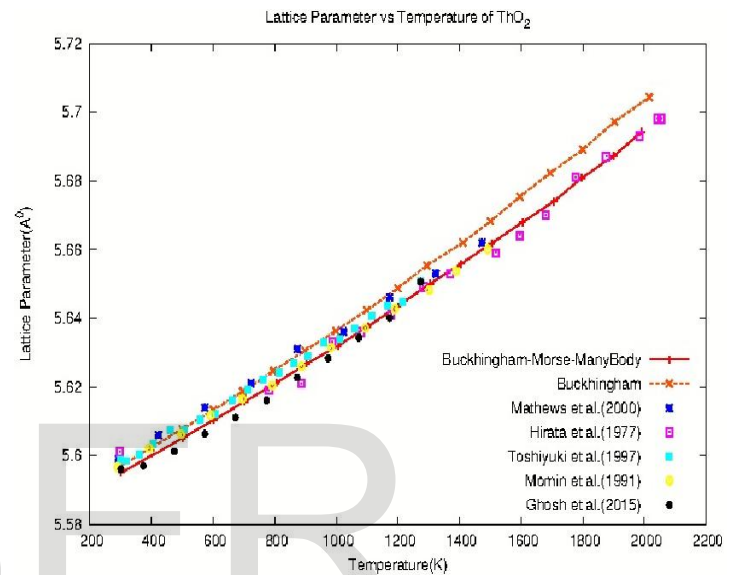


Fig.3. Lattice Parameter vs Temperature study from 300 K to 2000 K with various experimental data available for ThO₂.

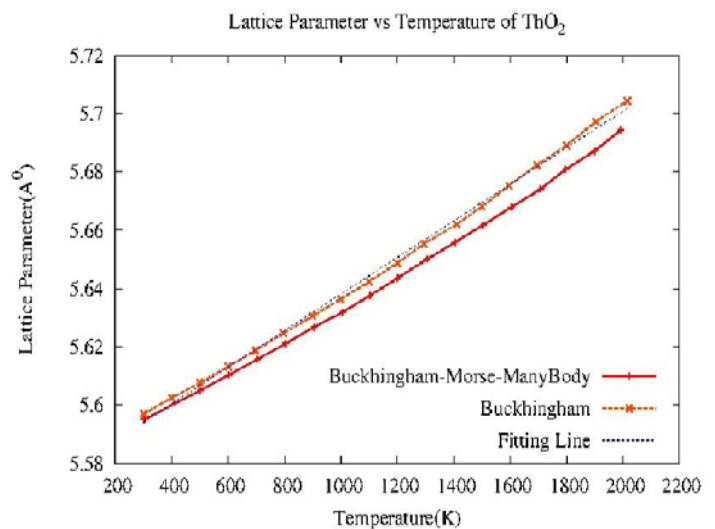


Fig.4. Fitting Curve drawn for finding the thermal expansion coefficient.

3.4. Specific Heat Capacity

Specific heat capacity of pure ThO₂ has been determined based on the enthalpy increment in Jmol⁻¹ values plotted

against temperature in K. Now, fitting a non-linear function of the type $f(x) = a + bx + cx^2 + dx^3 + ex^4 + fx^{-1}$, and using $C_p = \left(\frac{\partial H}{\partial T}\right)_p$, C_p is computed. Refer Fig.5.

Table 2. The values of the constants came out for Buckingham Potential as:

Constants	This study	Experimental Values [4]
a	-7.970258 Jmol ⁻¹	-20.58 Jmol ⁻¹
b	40.6428 Jmol ⁻¹ K ⁻¹	51.68 Jmol ⁻¹ K ⁻¹
c	37.065 Jmol ⁻¹ K ⁻²	39.77 Jmol ⁻¹ K ⁻²
d	-17.29643 Jmol ⁻¹ K ⁻³	-21.63 Jmol ⁻¹ K ⁻³
e	3.4088 Jmol ⁻¹ K ⁻⁴	4.15 Jmol ⁻¹ K ⁻⁴
f	-2.14609 Jmol ⁻¹ K	1 Jmol ⁻¹ K

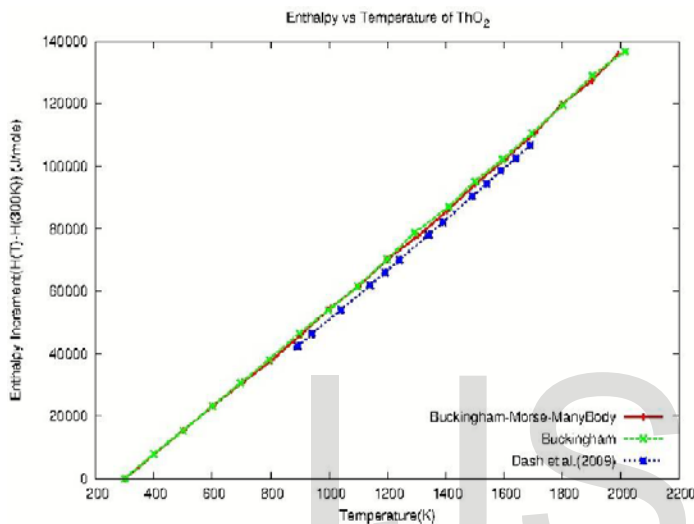


Fig.5. Enthalpy Increment (J/mol) vs Temperature (K) curve with the two potentials used for simulation with an experimental data.

3.5. Super-ionic Transition

3.5.1. From MSD studies

MSD calculations were carried out for ThO₂ at the two potentials (Buckingham and Buckingham-Morse-Many-Body) for 2592 atoms (6X6X6 supercell of ThO₂ unit cell) for 25 ps for a temperature range of 2500 K to 3500 K at an interval of 100 K. Using Buckingham Potential for a temperature range of 2900 K to 3400 K. Refer Fig.6. and Fig.7. It was observed that below 2600 K, the MSD calculations for oxygen showed that with increasing temperature, the MSD rises by a small amount. However, after a certain temperature (near 2700 K), there is a sudden large change in the MSD of oxygen atoms. This jump is associated with the creation of oxygen Frenkel defects at high temperatures and the super-ionic transition that the oxygen sub-lattice undergoes as this disorder proceeds. For Buckingham Potential, this jump came at 3000 K. However, for Buckingham-Morse-Many-Body, it came near 2600 K.

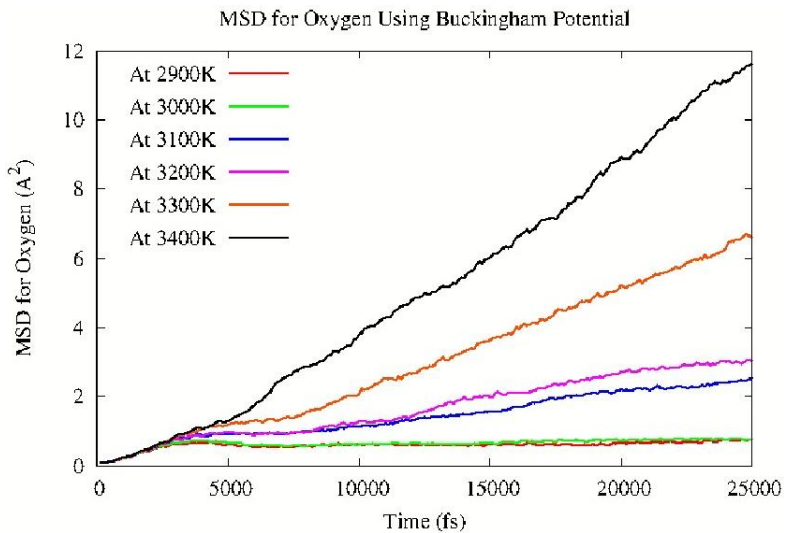
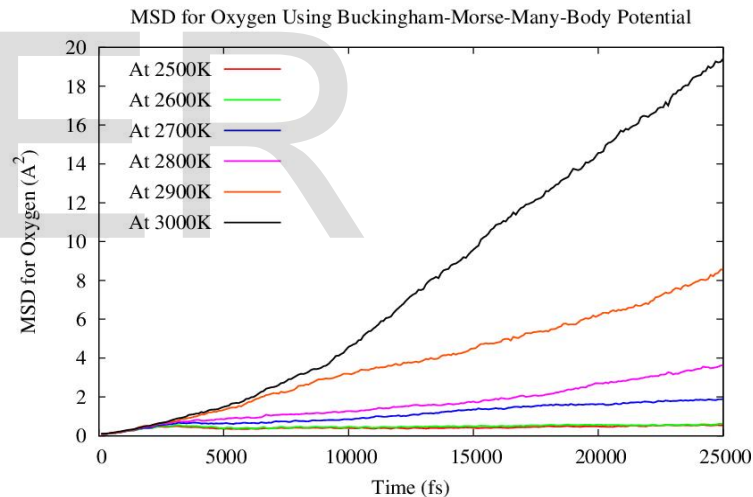


Fig.6. MSD curve for Oxygen using Buckingham Potential for a temperature range of 2900 K to 3400 K. The transition is visible at 3000 K.

Fig.7. MSD curve for Oxygen using Buckingham-Morse-Many-Body Potential for a temperature range of 2500 K to 3000 K. The transition is visible at 2600 K.



Many-Body Potential for a temperature range of 2500 K to 3000 K. The transition is visible at 2600 K.

3.5.2. From RDF studies

RDF calculations for Oxygen-Oxygen were carried out for ThO₂ at the two potentials (Buckingham and Buckingham-Morse-Many-Body) for 2592 atoms (6X6X6 supercell of ThO₂ unit cell) for 25 ps for a temperature range of 2500 K to 3500 K at an interval of 100 K. The change in the appearance of peaks within the cut-off distance indicated melting of the O-O sub-lattice, i.e. Super-Ionic Transition. For Buckingham Potential set, the range came out to be 2800 to 3300 K. For the Buckingham-Morse-Many-Body Potential set, the range came out to be 2600 to 3000 K. Refer Fig.8. and Fig.9.

RDF for O-O Using Buckingham Potential

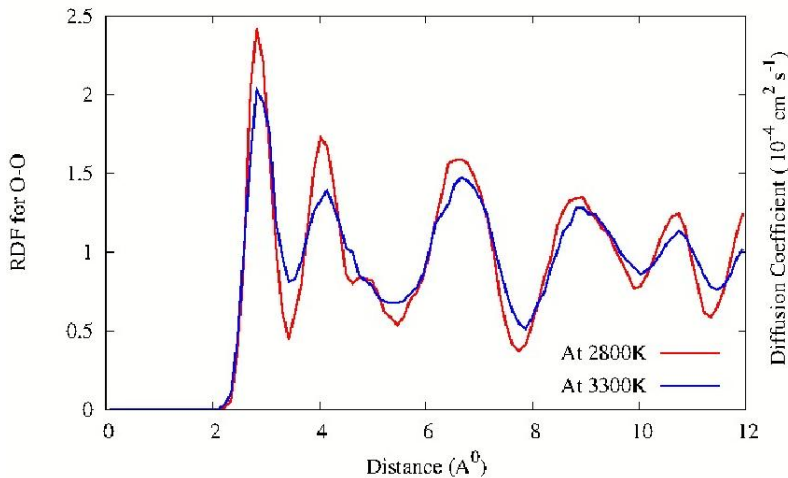


Fig.8. RDF curve for O-O pair using Buckingham Potential for a temperature range of 2800 K to 3300 K.

Diffusion Coefficient Using Buckingham Potential

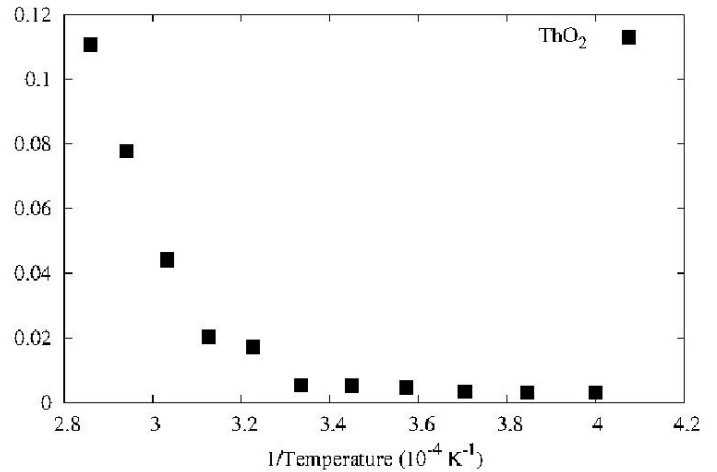


Fig.10. Diffusivity plot for oxygen using Buckingham Potential for a temperature range of 2500 K to 3500 K. The jump appears at 3000 K.

RDF for Oxygen Using Buckingham-Morse-Many-Body Potential

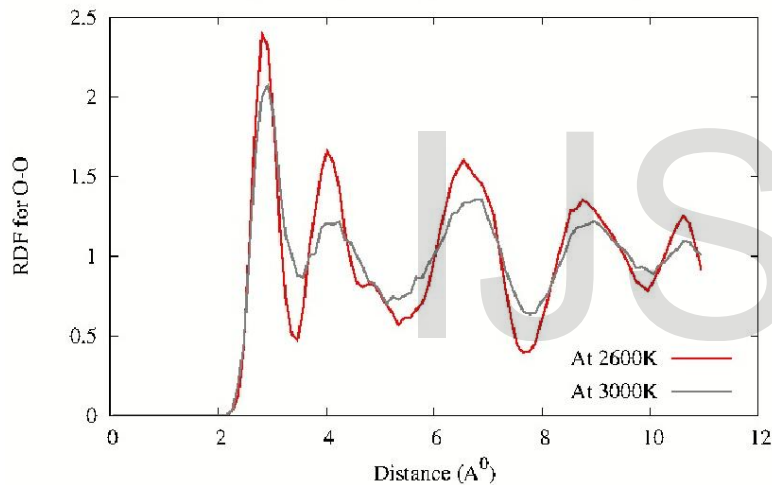


Fig.9. RDF curve for O-O pair using Buckingham-Morse-Many-Body Potential for a temperature range of 2600 K to 3000 K.

Diffusion Coefficient Using Buckingham-Morse-Many-Body Potential

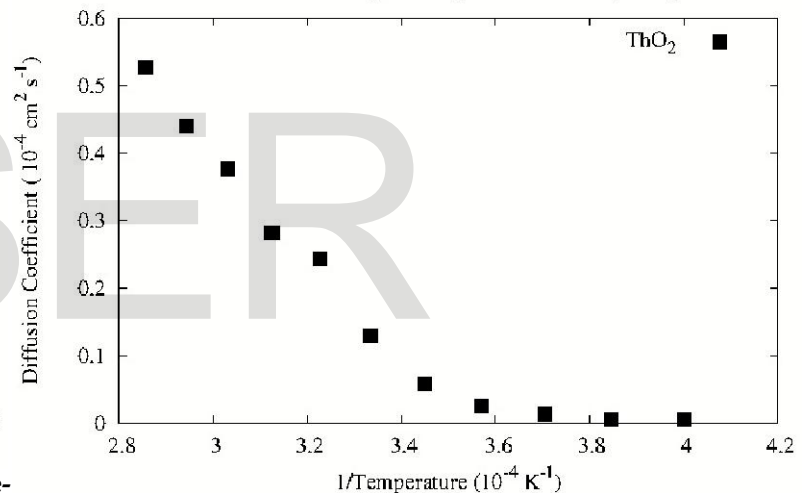


Fig.11. Diffusivity plot for oxygen using Buckingham-Morse-Many-Body Potential for a temperature range of 2500 K to 3500 K. The jump appears at 2800 K.

3.5.3. From Diffusivity values

Beyond the Super-ionic transition the oxygen sub-lattice exhibits a near liquid structure, thus, accounting for the change in diffusion regime. It can be observed from the figures given below that the diffusivity values show a minimal change near low temperature values. However, later there is a sudden hike in the diffusivity value occurring due to melting of oxygen sub-lattice. The simulation was carried out for ThO₂ at the two potentials (Buckingham and Buckingham-Morse-Many-Body) for 2592 atoms (6X6X6 supercell of ThO₂ unit cell) for 25 ps for a temperature range of 2500 K to 3500 K at an interval of 100 K and diffusivity was calculated from MSD data for oxygen. From the plot, in Buck potential, the temperature is nearly 3000 K and for B-M-MB potential, the temperature came out to be 2800 K. Refer Fig.10. and Fig.11.

3.6. Melting Point

The melting point range has been calculated on the basis of Two-Phase Simulation. For buck potential, the range is 3800-3825 K and for B-M-MB potential, it was 3650-3675 K. Clearly, the comparison with the experimental values shows that B-M-MB predicts a more close value.

For B-M-MB potential, refer to Fig.12. and Fig.13.
 For Buck potential, refer to Fig.14.

Potential	MD calculated temperature range (K)	Experimental values (K)
Buckingham	3800-3825	3573±100 Wartenberg <i>et al.</i> [5]
B-M-MB	3650-3675	3663±100 Benz <i>et al.</i> [6] 3651±17 Ronchi <i>et al.</i> [7]

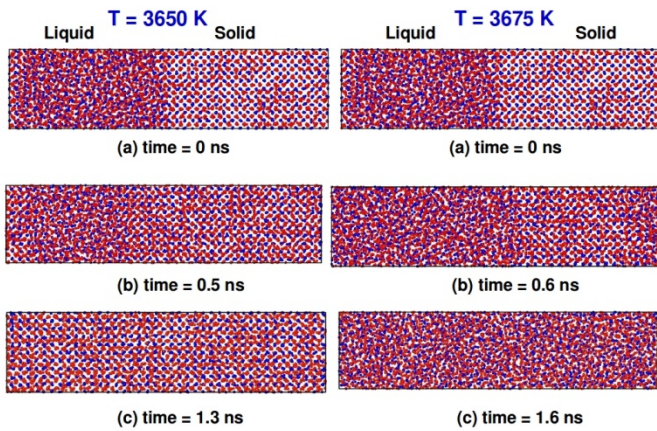


Fig.12. At T=3650 K, (a) An NPT ensemble is constructed containing 5184 atoms with half the region in liquid phase (at 4000 K) and the other half in solid phase (at 3000 K), (b) After 5,00,000 time-steps, the solid region is found to expand and fill the liquid region completely in as shown in (c) at 13,00,000 time-steps. At T=3675 K, (a) Another NPT ensemble is constructed containing 5184 atoms with half the region in liquid phase (at 4000 K) and the other half in solid phase (at 3000 K), (b) After 6,00,000 time-steps, the liquid region is found to expand and fill the solid region completely in as shown in (c) at 16,00,000 time-steps. The red dots here represent Th atoms and the blue dots represent O atoms.

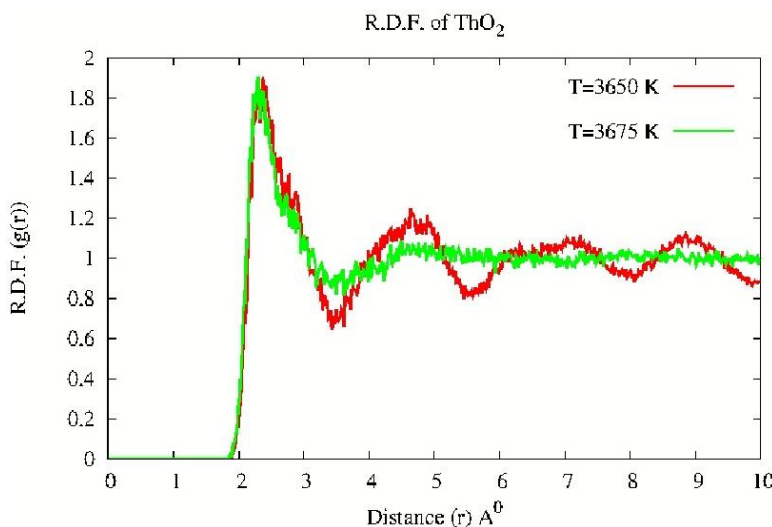


Fig.13. The difference in RDF plots at 3650 K and 3675 K shows a change in phase (from solid to liquid).

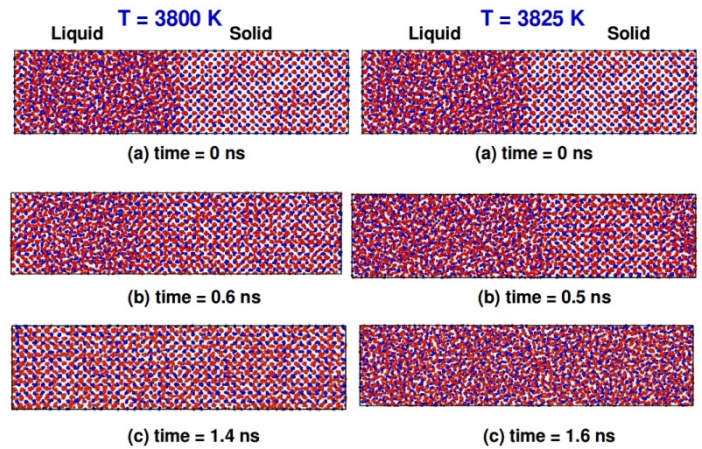


Fig.14. At T=3800 K, (a) An NPT ensemble is constructed containing 5184 atoms with half the region in liquid phase (at 4000 K) and the other half in solid phase (at 3000 K), (b) After 6,00,000 time-steps, the solid region is found to expand and fill the liquid region completely in as shown in (c) at 14,00,000 time-steps. At T=3825 K, (a) Another NPT ensemble is constructed containing 5184 atoms with half the region in liquid phase (at 4000 K) and the other half in solid phase (at 3000 K), (b) After 5,00,000 time-steps, the liquid region is found to expand and fill the solid region completely in as shown in (c) at 16,00,000 time-steps. The red dots here represent Th atoms and the blue dots represent O atoms.

Clearly, Buck potential predicts a temperature range higher than the experimentally obtained whereas B-M-MB predicts very close to the experimental range.

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